

LiVGe₂O₆, an anomalous quasi 1D, $S = 1$ system, as revealed by NMR

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We report the results of ^7Li nuclear magnetic resonance (NMR) studies of LiVGe_2O_6 , a quasi one-dimensional spin $S = 1$ model system, at low temperatures. Our data, including NMR spectra and the temperature dependence of the spin-lattice relaxation rate T_1^{-1} , indicate a first order phase transition to occur at $T_c \simeq 23$ K. The NMR response of LiVGe_2O_6 below T_c suggests that the ordered phase is antiferromagnetic and has unusual features. Possible reasons for this unexpected behavior are discussed.

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In recent years there has been considerable progress in the understanding of the physics of low-dimensional spin systems with an antiferromagnetic interaction between nearest-neighbor spins. For a quasi one-dimensional (1D) Heisenberg chain with integer spins, it is expected that the ground state is isolated from the excited states by an energy gap, the Haldane gap Δ_H [1]. This has indeed been observed in many systems [2]. For the case of monoclinic AgVP_2S_6 , where the V^{3+} ions with $S = 1$ form 1D chains along the a -axis, Δ_H is equal to 26 meV [3,4]. A continuous spectrum of excitations is expected, however, if the spins are half-integers. In this case the system may lower its energy via a spin-Peierls second order phase transition, again resulting in the opening of a gap, as observed for CuGeO_3 [5]. Here, the localized spins of the Cu^{2+} ions form 1D Heisenberg chains. A spin-Peierls transition is found at $T_{SP} = 14$ K, the resulting gap is of the order of 2 meV.

Last year a new member, LiVGe_2O_6 , was added to the growing list of 1D magnets by Millet and coworkers [6]. From the temperature dependence of the magnetic susceptibility $\chi(T)$ it was inferred that this $S = 1$ system does not behave as expected. A discontinuous change in $d\chi/dT$ at approximately 22 K was interpreted as a phase transition of the spin-Peierls type, and quantum chemistry calculations indicated [6,7] that this unexpected behavior might be due to the presence of a substantial biquadratic exchange interaction between the V^{3+} spins forming the infinite 1D chains. From these existing experimental data a more detailed analysis of the phase transition and of the nature of the low temperature phase was not possible.

In this Letter, we present a detailed ^7Li nuclear magnetic resonance (NMR) study invoking NMR spectra and spin-lattice relaxation rates. We also present new data on the magnetic susceptibility of LiVGe_2O_6 . We confirm that this system ought to be regarded as an $S = 1$ quasi one-dimensional Heisenberg spin system but the character of our NMR data is substantially different from that

of previously investigated 1D, $S = 1$ model systems [8,9]. Our results reveal very unusual low temperature properties, including a phase transition at 23 K which is not, as previously suggested, a second-order spin-Peierls transition to a dimerized phase, but rather a first-order phase transition to a magnetically ordered phase, rather unusual for a 1D, $S = 1$ system.

LiVGe_2O_6 crystallizes with a monoclinic structure, space group $\text{P2}_1/\text{c}$ [6]. The structure consists of isolated chains of VO_6 octahedra, joined at the edges. These chains are linked together and kept apart by double chains of distorted GeO_4 tetrahedra, keeping the inter-chain coupling small. The Li atoms are six-fold coordinated and are located inside distorted oxygen octahedra as in the case of LiVSi_2O_6 [10]. Our powder sample of 0.13 g was prepared as described by Millet et al [6].

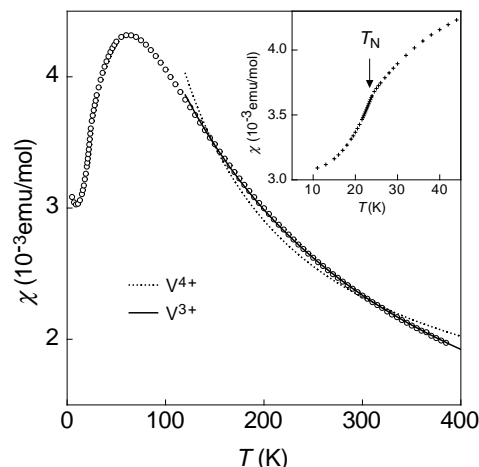


FIG. 1. Magnetic susceptibility χ as a function of temperature for LiVGe_2O_6 . The solid line represents the best fit to the data assuming a Curie-Weiss law for V^{3+} and the dotted line the corresponding fit for V^{4+} . The inset displays $\chi(T)$ in the region near the phase transition. The arrow indicates T_c .

An important issue concerning the basic physics of LiVGe_2O_6 is to verify that the V ions are in a trivalent oxydation state and hence $S = 1$. This claim is supported by our results for the electrical resistivity ρ which, measured on a sample prepared from pressed powder of LiVGe_2O_6 , was found to be larger than $2 \times 10^7 \Omega\text{-cm}$ at room temperature, indicating that LiVGe_2O_6 is indeed an insulator. Taking into account the known oxydation states of O^{2-} , Li^{1+} , and Ge^{4+} , the valence of V must be +3. Further support for this simple, yet important clarification is provided by the results of the magnetic susceptibility $\chi(T)$ (Fig. 1). Our results are similar to those of Ref. [6], albeit with a smaller paramagnetic contribution at low temperatures. The high temperature part of $\chi(T)$ can reasonably be fitted only by assuming a trivalent configuration of V. The phase transition, suggested by a kink in $\chi(T)$ at $T_c = 23 \text{ K}$ (see inset to Fig. 1), is much more evident by plotting $d\chi/dT$ versus T , as demonstrated in Fig. 2. The well defined maximum is only weakly, if at all, shifted by an external magnetic field. The upturn of $\chi(T)$ at the lowest temperatures is associated with a small amount of paramagnetic impurities (a few parts per mil of $S = 3/2$) and will not be considered further.

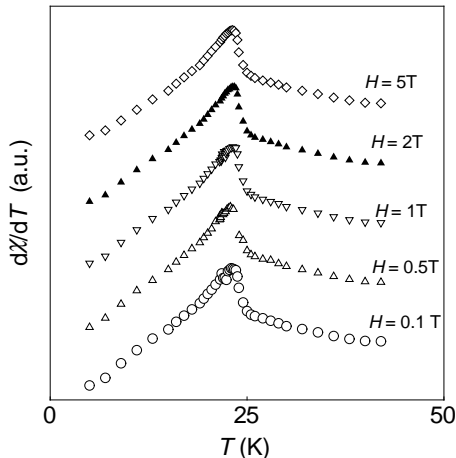


FIG. 2. $d\chi/dT$ as a function of the temperature for different applied fields. The clear maximum in $d\chi/dT(T)$ signals the transition temperature T_c .

In Fig. 3 we show three examples of the ^7Li NMR (nuclear spin $I = 3/2$) spectra measured at a fixed frequency of 70.64 MHz and at temperatures of 15.8, 22.0 and 24 K. For these measurements a two-pulse spin-echo sequence was employed and the data represents the integrated spin-echo intensity. An example of the NMR spectrum for randomly oriented powder of LiVGe_1O_6 at 39 K is shown in the inset of Fig. 3. This data was acquired at a fixed applied field of 4.28 T. This spectrum reveals the absence of quadrupolar wings, and its shape indicates an anisotropic shift. The maximum intensity and the prominent shoulder correspond to grains where the Li sites have their quadrupolar axis orthogonal and

parallel to the applied field, respectively. Below 30 K the shape of the signal develops into a well defined and symmetrical line with a width (HWHM) of approximately 35 Gauss (see the NMR spectrum at 24 K), which we take as evidence for the alignment of the grains of our powdered sample in the presence of applied magnetic fields of the order of a few Tesla at low temperatures. Another scenario where the observed changes in the NMR spectrum simply reflect changes in the susceptibility and/or hyperfine field coupling, yielding an isotropic line shift below 30 K, cannot really be ruled out.

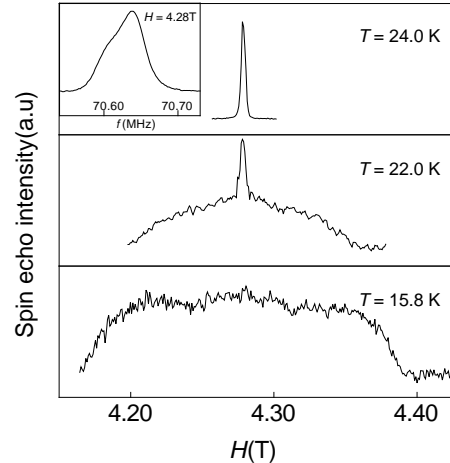


FIG. 3. ^7Li NMR spectra of LiVGe_2O_6 measured at a fixed frequency of 70.64 MHz for three different temperatures. Below 23 K the ^7Li -NMR spectrum becomes very broad. The inset to the top figure shows the ^7Li NMR spectrum measured at a fixed applied field of 4.28 T and 39 K.

From the NMR line shift K data (not shown here) we estimate the hyperfine field at the Li nuclei to be of the order of 0.65 kG per μ_B of V magnetic moment. This value seems consistent with a direct dipolar coupling between the V magnetic moments and the Li nuclei and we conclude that the ^7Li NMR response is dominated by the magnetism of the V ions. The temperature evolution of the NMR spectrum above 23 K shows no indication of a gap in the spectrum of excitations of the spin system.

At temperatures below T_c the NMR spectrum changes dramatically and its width increases very rapidly with decreasing T . At temperatures not far below T_c (see the spectrum for 22 K in Fig. 3) we note the coexistence of two phases. The narrow line, related with the high-temperature paramagnetic phase, appears on top of a broad background representing the low-temperature phase. At even lower temperatures only the signal due to the low temperature phase is measured. This behavior is compatible with a first order phase transition at T_c but not with a second order phase transition such as a standard spin-Peierls transition or a simple magnetic ordering phenomenon. In particular, one also may argue that the coexistence of the two phases is due to a

spread of transition temperatures within the sample material [11]. In the latter case it would seem quite unlikely to observe the distinct peak in the temperature variation of T_1^{-1} , displayed in Fig. 4.

On the basis of the presently available experimental data, nothing definitive can be said concerning the nature of the low temperature phase. The broad NMR spectrum may either represent the powder spectrum of a distorted antiferromagnetically ordered phase or, in case that the powder grains are indeed aligned at low temperature, a modulated magnetic structure is also conceivable. Further experiments on single crystals will have to answer this question.

In order to probe the low-energy spin excitations in LiVGe_2O_6 at low temperatures, we measured the spin-lattice relaxation rate T_1^{-1} by monitoring the recovery of the ^7Li nuclear magnetization after the application of a long comb of rf pulses above and below T_c . Both above and below T_c a single exponential recovery was observed, the first as expected and the latter in spite of the fact that the NMR spectrum is very broad and hence cannot fully be irradiated. Various changes of irradiation conditions yielded, within the usual error limits, identical results for T_1^{-1} , however.

In Fig. 4 we display the temperature dependence of the spin-lattice relaxation rate. A prominent peak in $T_1^{-1}(T)$ reflects the phase transition at T_c . Above T_c , T_1^{-1} varies only weakly with temperature, a further evidence for the absence of a significant energy gap in the spin excitation spectrum. For an insulator the relaxation rate is very high and is most likely caused by fluctuations of the localized V-ion moments. Below T_c , T_1^{-1} decreases very rapidly, signalling the opening of a gap in the spectrum of spin excitations. From the relaxation data between 17 and 10 K, we calculate a gap $\Delta/k_B = 83$ K, obviously a feature of the low temperature phase.

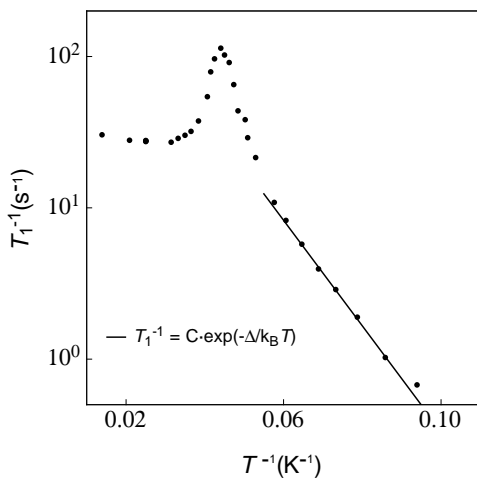


FIG. 4. Temperature dependence of the ^7Li spin-lattice relaxation rate in LiVGe_2O_6 . Above 28 K T_1^{-1} is only weakly T -dependent, but at low temperatures T_1^{-1} decreases exponentially with decreasing temperatures.

The magnitude of this gap is very surprising because it is substantially larger than the estimated exchange interaction J above T_c . For standard $S = 1$ chain systems, the maximum of the susceptibility at 60 K would imply that, for the high temperature phase, $J/k_B \approx 45$ K. This suggests that some kind of modification, presumably involving the crystal structure, takes place at the transition, changing the local quantum chemistry and enhancing the exchange interaction. In case of a standard transition to magnetic order with $J/k_B \approx 45$ K, and recalling that the anisotropy D/k_B is smaller than 20 K [6], the spin-orbit gap would be of the order of $(2DJ/k_B^2)^{1/2}$, i.e., at most 40 K.

The unexpected properties of LiVGe_2O_6 , not typical for quasi 1D, $S = 1$ systems, are very likely related to the three t_{2g} orbitals accommodating the two $3d$ electrons of V^{3+} , as for V_2O_3 [12]. The orbital d_{xz} , which is separated from the other two by a second order crystal-field splitting Δ_{CF} due to the trigonal distortion [6], may modify the usual description in terms of a Heisenberg model in two ways.

If Δ_{CF} significantly exceeds the hopping integrals between neighbouring sites, the low-energy physics can still be described by a pure spin Hamiltonian. However, the third orbital gives rise to a ferromagnetic exchange channel. The Heisenberg coupling may thus considerably be reduced and other exchange couplings, such as a biquadratic interaction J'' between nearest neighbours or a bilinear exchange J_2 between next-nearest neighbours may become significant. In that case, the high temperature magnetic properties of the system would be described by the Hamiltonian

$$H = \sum_i [J' \mathbf{S}_i \cdot \mathbf{S}_{i+1} + J'' (\mathbf{S}_i \cdot \mathbf{S}_{i+1})^2 + J_2 \mathbf{S}_i \cdot \mathbf{S}_{i+2}] . \quad (1)$$

While the properties of the Hamiltonian of Eq. (1) with a frustrating next-nearest neighbour coupling have not been investigated yet, it is likely that the frustration due to J_2 will lead to incommensurate fluctuations, as in the case $J'' = 0$ [13], or the biquadratic interaction J'' will tend to close the Haldane gap, as in the case of $J_2 = 0$ [14,15]. With $J''/J' \simeq 1$ and $J_2/J' > 0.35$, we conjecture that this Hamiltonian leads to a very small gap and to incommensurate fluctuations. This might provoke a spin-Peierls type instability to an incommensurate phase and explain part of our results. Whether the transition can be of first order remains to be seen.

If Δ_{CF} adopts similar values as the hopping integrals, it will no longer be possible to describe the low energy properties of the system with a pure spin Hamiltonian, and the orbital degrees of freedom have to be included explicitly. The canonical example is V_2O_3 , and the properties reported here are reminiscent of the phase transition observed in insulating $\text{V}_{2-x}\text{Cr}_x\text{O}_3$ between the high-temperature paramagnetic and the low-temperature antiferromagnetic phase [12]. In particular, this transition,

due to an orbital ordering of the t_{2g} orbitals, is strongly first-order and there is a dramatic change of exchange integrals at the transition. If an orbital ordering takes place in LiVGe_2O_6 , it will quite likely also provoke a first order transition. The nature of the low temperature phase will depend on the effective spin Hamiltonian, hence on the orbital ordering. The possibilities range from a dimerized ground state involving a simple antiferro-orbital ordering with alternating exchange couplings, to more exotic phases including incommensurate phases if the orbital ordering is helical. In that case, the large gap would just be the spin-orbit gap, the exchange integrals being much larger than in the high temperature phase because of the orbital ordering. Further investigations testing the orbital occupancy on the V^{3+} ions are clearly needed to check this possibility. Unfortunately the shape of the low temperature NMR spectra does not allow for firm conclusions with regard to orbital ordering.

In summary, our results for LiVGe_2O_6 strongly suggest that this material is a very unusual 1D, $S = 1$, Heisenberg system. In particular the Haldane phase is either absent or strongly suppressed, and a first order phase transition into a magnetically ordered phase occurs at 23 K. On the theoretical front we have argued that this behavior is probably related to the second order splitting of the t_{2g} orbitals, which could either induce significant biquadratic and next-nearest neighbor exchange interactions along the chain, or provide an orbital degree of freedom which is involved in the ordering. Further investigations of the low-temperature phase and of the theoretical models are obviously needed to answer the questions that have been raised by our observations.

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